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- (54) MEDIUM FOR INK-JET RECORDING

TINTENSTRAHLAUFZEICHNUNGSMATERIAL

MATÉRIAU POUR IMPRESSION A JET D'ENCRE

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FP 1 040 935 R1

Description

Technical Field

[0001] The present invention relates to recording media, and in particular, relates to recording media for ink jet printers, in which ink absorptivity is superior, surface strength is superior, there is no decrease in density and no changing in color tone in direct sunlight or in room light, and in which ink is quickly absorbed, thereby satisfying future high speed printing technique requirements.

10 Background Art

- [0002] The use of ink jet printers is further increasing in recent years because they have characteristics such as vividness of recorded images, quiet operation, ease of coloring, and the like. In order to prevent the nozzle from being blocked due to drying of ink, an ink which is difficult to dry must be used in the ink jet printer. As ink having this property, water-soluble ink which is dissolved or dispersed with dye, solvent, additives, or the like, in water, is generally employed. However, a letter or an image formed on the recording medium by using the water-soluble ink in smore inferior to that in printed matter using pigment-type inks or to that in silver halide photographs from the viewpoint of water resistance, moisture resistance (having no color changing or fading even if the medium is left under high temperature and high humidity), and light resistance such as shelf-life in a room and resistance to direct sunlight.
- 20 (0003) In recent years, as ink jet printers become less expensive and high widness and colorfulness of printed mape is anticipated, the requirements for various properties such as light resistance of recorded images, surface strength or recording media for ink jet printers, etc., are gradually becoming severe. Therefore, completely satisfying these various requirements, such as light resistance, surface strength, etc., is an essential goal for recording media for his kjet printers. [0004] In conventional recording media for ink jet printers, improvements in light resistance of recordings of letters, images, etc., in particular, full color recordings, have been proposed; however, they are not yet sufficient. Furthermore, in the recording media for ink jet printers, an ink receiving layer containing many pigment components having superior ink absorbability is formed, and a large amount of ink is used in full color recordings. Surface strength of the ink receiving.
- layer is thereby deteriorated, so that there are problems with respect to surface strength, such as flaking off of the pigment, or peeling of the ink receiving layer, when the media are rubbed on the surface or are bent. 10 (1005) JP-A-100/29369 discloses an ink-jet-receiver sheet comprising an ink-receiving layer provided on a base material, wherein the said ink-receiving layer contains an acrylic copolymer formed by copolymerizing at least three components selected from the monomers (meth)lacrylate hydroxysykly (meth)acrylate and an antioxidation monomer and/or
 - an ultraviolet absorbing monomer.

 [0006] JP-A-61/42/2871 discloses a recording material with an ink-receiving comprising a copolymer having the components: ethylacrylate, hydroxyethyl methacrylate and 2-oxy-4-(2-oxy-3-methacryloxy) hydroxyethyl methacrylate as residable ultraviolet absorbing acent.
 - [0007] JP-A-08/169172 discloses an ink jet recording sheet in which a copolymer containing a monomer having ultraviolet ray absorbability is incorporated into neutralized paper.
 - [0008] JP-A-08/080662 discloses an ink jet recording paper in which a copolymer containing methyl methacrylate and 2-hydroxyethyl (metha)acrylate are contained in an ink receiving layer.
 - [0009] It is an object of the present invention to provide a recording medium for ink jet printers having superior recording properties for ink jet printers, and having superior light resistance, which did not exist in the past, and having superior surface strengths on that recorded images are not easily begled off.
- [0010] The inveniors have conducted various research with regard to recording media for ink jet printers, and have found that the light resistance and the surface strength of the recording media for ink jet printers are improved very effectively by providing an ink receiving layer containing an acrylic type copolymer in which (metha)acrylate, hydroxyalkyl (metha)acrylate, and antioxidation monomers and/or ultraviolet ray absorption monomers are copolymerizing components.
- [0011] Therefore, a recording medium for ink jet printers according to the present invention has been made on the basis of the above knowledge, and it is characterized in that an ink receiving layer is provided on a base material, the ink receiving layer contains an acrylic type copolymer comprising four components of an A component: (metha]acrylate, a B component: hydroxyalkyl (metha]acrylate, a C component: antioxidation monomer and/or ultraviolet ray absorption monomer, and acrylonititie as a copolymerizing component.
- [0012] A recording medium for ink jet printers according to the present invention has a structure in which at least one on ink receiving layer is laminated on at least one surface of a base material by a laminating method such as a coating method, and the ink receiving layer may consist of two or more layers. If it consists of two or more layers, the acrylic type copolymen of the present invention may be contained in a least either of the layers.
 - [0013] A preferable embodiment according to the present invention has a structure in which two or more ink receiving

layers are laminated. A first embodiment is characterized in that the acrylic type copolymer of the present invention is contained in a first link receiving layer being on a base material side and a second embodiment is characterized in that it is contained in a second ink receiving layer being on a surface side, and these will be explained in detail. The above first ink receiving layer and second ink receiving layer may consist of two or more layers, respectively.

- [0014] In the first embodiment, the A component (metha)acrylate is preferably alkyl acrylate, and in the second embodiment, its preferably falkylamion alkyl methacrylate. Furthermore, in the second embodiment, not only the above A, B, and C components, but also acrylamide, must be contained as an essential copolymerizing component of the acrylic type copolymer.
- 1. First Embodiment
 - (1) Base Material

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- [0015] As a base material provided for an ink receiving layer according to the present invention, a base paper which is mixed wood puip, such as a chemical pulp such as LBKP, NBKP, or the like; etc., or synthetic fiber pulp such as polyethylene fiber, or the like, as a primary component, with pigment and any type of additive which is typically employed in paper, such as sizing agents, yield improving agents, strengthening agents, or the like, alone or in combination, as necessary, and produced by using any type of paper-making apparatus such as a fourdniner paper machine, cylinder paper machine, twin wire paper machine, or the like, can be preferably employed. In addition, a base paper provided with starch, polyvinyl alcohol, or the like using a size press; a base paper provided with an anchor coat layer; a coated paper, such as art paper, coated paper, cast coated papers, can preferably be employed. These base papers and coated papers was be provided with an anchor coat layer or these base papers, can preferably be employed. These base papers and coated papers may be provided with an ink receiving layer directly, and a paper controlled flattening before coating the link receiving layer, using a calender apparatus such as a machine calender. To calender, soft calender coating the link receiving layer, using a calender apparatus such as a machine calender. To calender, soft calender coaten the like was the employed.
 - [0016] As a base material, a polyolefin resin layer may be provided on the surface of the above-described base paper, and synthetic resin such as polyethylene, polypropylene, polyester, nylon, rayon, polyurethane, or the like; film material comprised of mixture with these: and fiber-formed media of these synthetic resins may be employed.
- 30 (2) First Ink Receiving Layer

[0017] In this embodiment, as a main component of the binder resin in the first ink receiving layer provided on the base material, acyricit type copylower in which at least three components consisting of the A component: ally a crylste, the B component: hydroxyalkyl (metha) acrylate, and the C component: anisoxidation monomer and/or ultraviolet ray absorption monomer are copylometrizing components, is, employed. Superior recording properties for ink, let printers can thereby be attained. The first ink receiving layer is formed by adding other binder resins or additives to this acrylicitype copolymer and obtiment as necessary.

- (a) Copolymerizing Component of Acrylic Type Copolymer
- [0018] Alkyl acrylate of the above A component has effects on film strength, miscibility with pigments, stability of the coating material, etc., and a sikyl acrylate, a chemical compound shown in the following chemical formula 1 and be employed. The content of alkyl acrylate in the acrylic type copolymer is preferably 50 mole % or more. If it is less than 50 mole %, the film strength is insufficient, thereby causing a problem in wear resistance. In the chemical formula 1, R1, refers to an alkyl group having one to six carbon atoms, and especially, ethyl acrylate is preferable in the present invention since it has superior moisture resistance in which color of images do not change or fade even if recorded images are left under high temperature and high humidity.

Chemical Formula 1 CH₂=CH

[0019] As the hydroxyalkyl (metha)acrylate of the above B component, a chemical compound shown in the following chemical formula 2 can be employed, Hydroxyalkyl (metha)acrylate has an effect in which the dispersibility of the acrylic

type copolymer increases and the dainty or the light resistance of images is improved. The content of the B component in the acrylic type copolymer is preferably 1 to 25 note %. If this content of the B component is more than 25 note %, a problem occurs in that the water resistance is inferior. In the chemical formula 2, R₂ refers to a hydrogen attorn or a methyl group, R₃ refers to an alkyl group having one to six carbon atoms having a hydroxyl group as a substituent, and it is preferable that this hydroxyl group be in the terminal group. Of these compounds, 2-hydroxyethyl methacrylate is preferably employed in the present invention since the above effect is particularly superior.

Chemical Formula 2

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R₂ CH₂=C COOR₂

[0020] Antioxidation monomer and ultraviolet ray absorption monomer of the above C component has a structure which can polymerize with the above A component and B component. As these monomers, chemical compounds in which a water solubility and a dispersibility are superior, for example, chemical compounds shown in the following chemical formula 3 (antioxidation monomer), and chemical compounds shown in the following chemical formula 4 (ultraviolet and the proposed shore or in combination, respectively. However, at least one compound must be contained in the copolymer. Thus, since antioxidation monomer and/or ultraviolet ray absorption monomer are included in the activity type copylemer, the obtained light resistance is even more superior than the case in which antioxidant and/or ultraviolet ray absorbting agents are only added to the binder resin. The content of the C component in the acrybic type copyleme is preferably 1 to 22 mole %. If it is more than this range, the image characteristic, in particular, the link absorptivity, is deteriorated. In the chemical formulas 3 and 4, R, refers to a hydrogen atom or an alkyl group, R are fers to a hydrogen atom, a methyl group, or an elkyl group. R are fers to a hydrogen atom, a nearly group, or an acytoxy group, or an alkyl group, an acytoxy group, or an alkyl group has oriestably one to three carbon atoms.

Chemical Formula 3

Chemical Formula 4

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$$\begin{array}{c} \bigcap_{c} A \\ CH_2 = \bigcap_{c} C \\ CO - NH \\ (CH_2)_B \\ NH - CO - \bigcap_{c} A \\ R_6 \end{array}$$

$$CH_2 = C$$
 COO
 N
 N
 $(I = 0, 1, or 2)$

$$CH_2 = C$$
 $CONH^-(CH_2)_8 - O$
 $(R_6)_m$
 $(m = 0, 1, 2, or 3)$

[0021] As copolymerizing components of the ecylic type copolymer other than the above A, B, and C components, chemical compounds which do not deteriorate the dispersibility of the acylic type coplymer and the miscibility with the binder resin and which improve the recording properties for ink jet printers, the light resistance, and the wear resistance, can be added in appropriate amounts. Acrylonitrile shown in the following chemical formula 5 is employed as a copolymerizing component.

Chemical Formula 5

(b) Preparation of Acrylic Type Copolymer

[0022] Since alkyl acrylate of the A component is slightly soluble in water, acrylic type copolymer is prepared by the above materiats using an emulsion polymerization method, and it is used as an emulsion. The above copolymerization component is dispersed in water with an emulsifiner, whereby the A component is taken in a micell which is formed by the emulsifiner, so that the emulsion is prepared. As an emulsifiner, at least one of an anionic type, cationic type, and non-ionic type surfactant is employed, generally. In the preparation of the acrylic type copolymer for the present invention, if partially saponified polyvinyl actohol. Next, radicals are generated in the water layer by adding a polymerization initiator to this emulsion, and polymerization is nitiated. Polymer radicals of low polymerization degree formed there can enter into the micell and can form polymers of high polymerization degree by further polymerizing with the A component. In this method, the rate of polymerization is high since the polymerization is carried out in the micell, and the polymer of high polymerization degree is easily obtained. Furthermore, distribution of molecular weight of the polymer for a prarrow, and roncelles of the acrylic copolymer are assilv controlled.

10023] Heating temperature for the polymerization is preferably 60 to 100°C, and is more preferably 80 to 90°C. When the heating temperature is tool ow, weight-average molecular weight increases extremely, whereby the ink absorptivity, etc., is deteriorated. In contrast, when it is too high, a normal polymerization reaction does not occur, whereby by-products are formed. If a polymer in which the weight-average molecular weight is low is used in a first ink receiving layer, the film strench thereof is insufficient.

[0024] As a polymerization initiator as described above, well-known radical polymerization initiators can be employed. Specifically, azo type initiators such as 2.2-azobis-zboutyfontnile, 2,2-azobis-2-methyl butyfontnile, 1,1-azobis-1-cyclohexane carbontrille, dimethy-2,2-azobis isobutylate, 2,2-azobis-2-methyl propane)-2-hydrochloride, or the like, and peroxide type initiators such as benzoyl peroxide, decanoyl peroxide, acetyl peroxide, t-butyl peroxide, octanoyl peroxide, succinyl peroxide, or the like can be employed. The half-life temperature of these initiators is preferably 60 to 5 90°C. and is more preferably 65 to 80°C.

(c) Binder Resin

[0025] As binder resin contained in a first link receiving layer according to the present invention, the above acrylic type copolymer is employed as a main component. The acrylic type copolymer is preferably 30 to 100% by weight to the overall binder resin, and is more preferably 40 to 80% by weight. As binder resin which can be employed with the acrylic type copolymer, water soluble or water-dispersive resins can be employed alone or in combination. For example, polyviny alcohol, modified polyviny alcohol, acrobide polyviny alcohol, but any cate to explore a complex of the filed starch, casein, gelatin, soybean protein; cellulose derivatives such as carboxymethyl cellulose, bydroxyethyl cellulose, or the like; onlygate diene type copolymer lates vanch as elated anybride resin, styrene-butadiene copolymer, methyl methyl methacrylate-butadiene copolymer, or the like; acrylic type polymer latex such as fembary acrylate polymer, (metha) acrylate copolymer, or the like; invylic type polymer latex such as althylene-vinylacetate copolymer, or the like involved in monomer including functional groups such as carboxy group, or the like of alt types of these polymers; water-soluble adhesive such as polymethylembarylate, polyurethare resin, unstand polymer to the like; acrylic resin type adhesive such as polymethylembarylate, polyurethare resin, unstand polysest resin, vinylchorde-vinylacetate copolymer, polyvinylbutyral, alkyd resin, or the like, can be preferably employed. These can be employed alone or in combination.

(d) Pigment

[0026] In a first ink receiving layer according to the present invention, generally used pigments which are insoluble or slightly soluble in water can be employed alone or in combination. For example, a white inorganic pigment such as precipitated calcium carbonate, heaving, take, calcium sulfate, braium sulfate, titanium dioxide, zinc oxide, zinc sulfide, zinc carbonate, satin white, aluminum slicate, datomite, calcium slicate, magnesium slicate, synthetic amorphous slica, colloida slica, colloida almian, pseudo-benimte, aluminum tyhordixel, alumina, lithopone, zeolite, hydrolytic halloysite, magnesium carbonate, magnesium hydroxide, or the like; an organic pigment such as styrene-type plastic pigment, acrylic-type plastic pigment, polyethylene, urea resin, melamine resin, or the like, etc., can be employed.

[0027] Of these pigments, as white pigment which is a primary component contained in a first link receiving layer, a porous inorganic pigment is preferable since drying properties and absorptivity of an ink for ink jet printers is superior. For example, porous synthetic amorphous silica, porous magnesium carbonate, porous alumina, or the like, are preferably employed. Of these, since both printing quality and shelf-life (water resistance, wear resistance, light resistance, shelf-life in direct sunichly are satisfed in the present invention, the precipitation type or the get lyee porous

synthetic amorphous silica with a specific surface of about 200 to 600 g/m² can be preferably employed. [0028] With respect to a compounding ratio of pigment and binder resin in the first ink receiving layer, binder resin to pigment is preferably 30 : 70 to 95 : 5 by weight ratio, and is more preferably 30 : 70 to 50 : 50 by weight ratio.

(e) Other Additives

[0029] In order to improved light resistance of images or various properties, a water-soluble divalent or greater metallic salt can be additionally included in a first lint receiving layer. Specifically, magnesium chloride, land unchoride, because unchoride, because the calcium suffate, magnesium chlorate, magnesium phosphate, magnesium nitrate, or the like, can be preferably employed. The metallic salt content to total solid of the first link receiving layer is preferably 1.0 to 40.0 % by weight. and is more preferably 5.0 to 20.0 % by weight. [0030] Furthermore, as other additives, pigment dispersing agents, thickners, flow improving agents, decided inhibitors, surface bufficants, founding agents, permetaring agents, concloyed, socior prigments, fluorescent brightening agents, Unional proving agents, Puttoning agents, Puttoning agents, Puttoning agents, Orthonic pagents, Orthonic

(f) Forming of First Ink Receiving Layer

[0031] A coating solution is prepared by dissolving or dispersing the above coating materials in water or a suitable solvent such as alcohol, which can dissolve the materials. The first link receiving layer is formed on a base material by coating the coating solution, using various kinds of apparatus such as a blade coater, roll coater, air knife coater, bar coater, roll bade coater, solven preparations of the coater, bar coater, roll bade coater, size press, or the like on-machine or not proprietal emounts. The first ink receiving layer may be one layer, or may consist of two layers, if the layer consists of two layers, the above copolymer may be contained into both layers, or may be contained into not his layers, or may be contained into the layer solven solven because the solven solven

[0032] The coating weight of the first ink receiving layer in the one layer type is preferably 5.0 to 3.00 g/m². In the case of the two layer type in which two first ink receiving layers are provided on a base material, the coating weight of the first layer is preferably 5.0 to 3.00 g/m², and is more preferably 5.0 to 2.00 g/m². In addition, the coating weight of the second layer is preferably 5.0 to 15.0 g/m², and is more preferably 5.0 to 10.0 g/m². In the case in which it is above this range, problems such as powering of the layer, decrease of productivity, increase in cost or the like occur. In particular, in the case in which it is above this range, problems such as powering of the layer, decrease of productivity, increase in cost or the like occur. In particular, in the case in which the coating weight of the second layers more than 15 g/m², it is difficult for the kit opass through to the second layer, thereby causing blurring of ink, so that vividness of images is impaired. Thus, it is preferable that the coating weight of the first ink receiving layer be controlled according to the number of the provide ink receiving layer may be finished using a calender such as a machine calender, TG calender, super calender, soft calender, or the like.

(3) Second Ink Receiving Layer

[0033] In the present invention, a second ink receiving layer which contains binder resin and jogment and which exists at surface side, can be provided on the above first ink receiving layer. As binder resin for forming the second ink receiving layer, water-soluble resins which can be used in the above first ink receiving layer, can be employed in appropriate amounts. In order to improve recording properties such as link absorptivity, etc., pigments which can be used in the above first ink receiving layer, or the referably contained with the above binder resin in the second ink receiving layer. Of the pigments, in particular, colloids silica is preferable, since it has superior dispersibility and has effects on improvement of the stability of coating materials and the productivity thereof.

[0034] As material for forming the second ink receiving layer, except the above binder resin and pigment, additives for improving light resistance of images and various properties used in the first Ink receiving layer can be mixed in appropriate amounts as necessary. With respect to a compounding ratio of binder resin and pigment in the second ink receiving layer, binder resin to pigment is preferably 5: 95 to 30: 70 by weight ratio, and is more preferably 5: 95 to 20: 80 by weight ratio.

20 : 80 by weight ratio.
[0035] A coating solution is prepared by dissolving or dispersing the above coating materials in water or a suitable solvent such as organic solvent. The second ink receiving layer is formed by coating the coating solution on a first ink receiving layer and drying, in the same manner as that of the first ink receiving layer. In the case in which it which the second ink receiving layer is directly provided on a base material, the coating weight of the second ink receiving layer is preferably 5.0 to 20 gm². In the case in which it is provided on the first link receiving layer, the coating weight is preferably 5.0 to 15.0 gm². And is more preferably 5.0 to 10.0 gm². When the coating weight is more than 15.0 gm². It is difficult for ink to pass through to the second ink receiving layer, thereby causing blurring of link, so that vividness of images is impaired. Furthermore, the second link receiving layer may be a glossy layer, and may be finished affer coating, using

a calender such as a machine calender, TG calender, super calender, soft calender, or the like.

- 2. Second Embodiment
- 5 [0035] The second embodiment according to the present invention differs from the above first embodiment in the structures of the first link receiving layer and the second ink receiving layer. In the following, differences between the first embodiment and the second embodiment will be explained in detail. Here, explanations of identical materials such as base materia, bioment, additives, etc. and identical means for forming the layers, were omitted.
- 10 (1) First Ink Receiving Layer

[0037] In a first ink receiving layer of the second embodiment, acrylic type copplymer is not an essential component, and water-soluble resine which can be used with the acrylic type copplymer in the first ink receiving layer of the first embodiment, can be employed as a binder resin. In addition, a compounding ratio of pigment and binder resin to the first link receiving layer is also different from the first embodiment, and binder resin to pigment is preferably 1: 1 to 1: 15 by weight Tailo. and is more preferably 1: 2 to 1: 10 by weight Tailo.

(2) Second Ink Receiving Laver

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- 20 [0038] A second ink receiving layer in the second embodiment according to the present invention is directly provided on at least one side of a base material or is further provided on the above first ink receiving layer which is provided on at least one side of a base material, as the most surface layer, in binder resin for forming the second ink receiving layer, acrylic type copolymer in which at least the A component: dialkylamino alkylmethacrylate, the B component: hydroxyalkyl (mitha)acrylate, the C component an altoxidation monomer and/or ultraviolet ray absorptivity monomer, and acrylonitrile as a sopolymerizing components, must be contained.
 - [0039] In order to improve the recording properties such as ink absorptivity, it is preferable that pigments used in the above first ink receiving layer be contained with the above arrylic type copdymer in the second ink receiving layer. Of the pigments, in particular, colloidal silica is preferable, since it has superior dispersibility and has effects in the improvement of the stability of coating materials and the productivity thereof. In the second ink receiving layer, the same materials as components of the first link receiving layer are no bused as necessary.
 - (a) Copolymerizing Component of Acrylic Type Copolymer
 - [044] Dialkylamino alkylmethacrylate of the above A component has effects on film strength, miscibility with pigments, stability of the coating material, etc., and as dialkylamino alkylmethacrylate, a chemical compound shown in the following chemical formula 6 can be employed. The content of dialkylamino alkylmethacrylate in the acrylic type copolymer is preferably 30 to 60 mole %, and is more preferably 40 to 50 mole %. In the chemical formula 6, Ry refers to an alkylene group having one to six carbon atoms, and Ry ferfers to an alkylene group having one to six carbon atoms; however, dimethylamino ethylmethacrylate is preferable in the present invention, since superior moisture resistance in which the color of images do not change or fade even if recorded images are left under high temperature and high humidity, and a uniform solution can be obtained when the acrylic type copolymer is prepared.

Chemical Formula 6

[0041] In the second embodiment, in order to further improve the water-solubility and the dispersibility of binder resin, or to maintain the miscibility with pigment, it is necessary that acrylamide be contained as an essential copolymerizing component of the acrylic type oppdymer, other than the above A, B, and C components. The content of acrylamide in the acrylic type oppolymer is preferably 2 to 7 mole %, and is more preferably 3.5 to 4.5 mole %. If the content is above this rance, light resistance is deteriorated.

[0042] As hydroxyalkyl (metha)acrylate of the above B component, a chemical compound shown in the following chemical formula 2 as described in the first embodiment, can be employed. Hydroxyalkyl (metha)acrylate has an effect

in which the water-solubility and the dispersibility of the acrylic type copolymer increases and the clarity and the light resistance of images is improved. Also in the second embodiment, 2-hydroxyethyl methacrylate is preferably employed, since the above effect is particularly superior. The content of the B component in the acrylic type copolymer is preferably 15 to 50 mole % and is more preferably 20 to 40 mole %. If this content of the B component is more than 50 mole %, a problem occurs in that the water resistance is inferior.

10043] Antioxidation monomer and ultraviolet ray absorption monomer of the above C component has a structure which can polymerize with the above A component and B component. As these monomers, chemical compounds in which the water-solubility and the dispersibility are superior, for example, chemical compounds shown in the following chemical formula 3 (antioxidation monomer) and chemical formula 4 (ultraviolet ray absorption monomer) as described in the first embodiment, can be employed. These compounds can be employed alone or in combination, respectively. However, at least one compound must be contained in the scrylic type copolymer. Also in this second embodiment, it is preferable that antioxidation monomer and/or ultraviolet ray absorption monomer be included in the water-soluble acrylic type copolymer. The content of the C component in the acrylic type copolymer is preferably 0.5 to 10 mole %. If it is above this range, the image characteristic, in actifular, the link absorptivity, is deteriorated.

[0044] Furthermore, as copolymerizing components of the acrylic type copolymer other than the above copolymerizing components, chemical compounds which do not deteriorate the water-solubility and the dispersibility of binder resin and the missibility with the binder resin and which improve the recording properties (or ink) let printers, the light resistance, and the wear resistance, can be added in appropriate amounts. For example, dimethoxy polyethyleneglycol methacrylate shown in the following chemical formula? Can be preferably employed as a pooplymerizing component, whereby more superior light resistance can be obtained in the second ink receiving layer. In chemical formula? In refers to an integer.

Chemical Formula 7

CH₃
I
CH₂=C
I
CO-(OCH₂-CH₃)-OCH

(b) Preparation of Acrylic Type Copolymer

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[0045] Preparation of the acrylic type copolymer can be carried out using a well-known general apparatus. The above copolymerizing components are dissolved in polymer/zation solvent; polymerization initiation is added in this solution; and then they are heated at 60 to 10°C, preferably at 80 to 90°C. Whereby, acrylic type copolymer in which weight-average molecular weight is several thousand to 100,000, preferably 10,000 to 20,000, is formed. When the heating temperature is too low, weight-average molecular weight increases extremely, whereby the ink absorphity; etc., is deteriorated. In contrast, when it is too high, a normal polymerization reaction is not generated, whereby by-products are formed. If a polymer in which the weight-average molecular weight is low is used in a second ink receiving layer, the film strendth threefol is instificient.

[0045] As a polymerization solvent as described above, water, alcohol, water-soluble ketone, and solutions of mixtures of these solvents can be employed. Of these solvents, mixed solution of water/alcohol is preferable, and in particular, a mixed solution of water/alcohol is preferable. With respect to the mixing ratio, ratio of water/alcohol is preferably 4/1 to 1/1, and is more preferably 2/1. As a polymerization initiator, well-known radical polymerization initiators for water-soluble acrylic resins can be employed. Specifically, initiators as described in the first embodiment can be preferably employed.

Best Mode for Carrying Out the Invention

[047] The effects according to the present invention will be illustrated by explanations of the Examples as and the Comparative Examples. As a base material, wood-free paper having a basic weight of 90.0 g/m / was employed in each Example and in each Comparative Example. The coating volumes of both a first link receiving layer and a second ink receiving layer were 10.0 g/m², in the Examples, the weight ratio of dried sold was used.

Example 1

Preparation of Acrylic Type Copolymer

5 [0448] 171 g of materials of acrylic type copolymer which removes B component from the following compounding, 0.72 g of potassium persulfate, and 7.2 g of partially saponified PVA (trade name: Kuraray Poval PVA-271 E; produced by Kuraray Co., Ltd.) as emulsifiner and protective colloid agent, were dispersed in 172.8 g of water, and this mixture was stirred at 3,000 rpm for 2 minutes, whereby an emulsion was prepared. 10 g of this emulsion was twisted with 0.18 g of potassium persulfate, 0.3 g of soldout hydrogenearbonate and 79.2 g of water, and was heated to 80±2°C in a floring an atmosphere. Next, a solution in which the rest of the above emulsion was mixed with 9.0 g of the following B component was added droywise to the heated mixture for 2 bours, and then the mixture was mixed with an agues solution in which 0.18 g of potassium persulfate was dissolved in 18 g of water, and was heated at 85 ± 2°C for 2 hours. This reaction solution was cooled and was adjusted to a pH value of 7 to 8 by aqueous ammonia, and then the solution was filtrated by a wire screen of 150 mesh, whereby a copolymer of acrylic-water emulsion having a weight-leverage for a confidence of the following copolymerization component at the following proportion, was greaared. Here, the compounding proportion of acrylic two condewer is shown by mole %.

Compounding of Acrylic Type Copolymer

[0049]

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- A component Ethylacrylate, 54.5 mole %
- B component
- 2-Hydroxy ethylmethacrylate, 13.4 mole %

 C component
 - UV absorptivity monomer represented by the following chemical formula 8, 1.0 mole %

Chemical Formula 8

Antioxidation monomer represented by the following chemical formula 9, 8.0 mole %

Chemical Formula 9

 Other component Acrylonitrile, 22.1 mole %

Forming First Ink Receiving Layer

[0050] Next, a coating solution for a first ink receiving layer of the following compounding was coated on one side of a base material, and was dried, whereby a first ink receiving layer was provided.

Coating Solution for First Ink Receiving Layer

[0051]

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10 • Binder resin

The above copolymer of acrylic-water emulsion (solid concentration: 41% by weight), 30 weight parts Itaconic acid modified PVA (trade name: KL-318 K; produced by Kuraray Co., Ltd.), 9 weight parts

- Silica (trade name: Mizukasil P78D; produced by Mizusawa Industrial Chemicals Ltd.), 39 weight parts
 Cationic dye fixing agent (trade name: Polyfix550; produced by Showa Highpolymer Co., Ltd.), 3.5 weight parts
- Magnesium chloride (trade name: Magnesium Chloride S; produced by Tomita Pharmaceutical Co., Ltd.), 2.5 weight parts
 - Water, 156 weight parts

Forming Second Ink Receiving Layer

[0052] Next, a coating solution for a second ink receiving layer of the following compounding was coated on one side of the above first ink receiving layer, and was dried, whereby a second ink receiving layer was provided. Therefore, a recording medium for link let printer according to the present invention was formed.

25 Coating Solution for Second Ink Receiving Layer

[0053]

- Partially Saponified PVA (trade name: Gohsenal T-330; produced by The Nippon Synthetic Chemical Industry Co.,
- Ltd.), 10 weight parts
 Colloidal Silica (trade name: Snowtex UP: produced by Nissan Chemical Industries, Ltd.), 90 weight parts

Examples 2 to 3. Reference Examples 4 and 5 and Comparative Examples 1 to 5

15 [0054] Recording media for ink jet printers of Examples 2 to 3 according to the present invention Reference Examples 4 and 5 and Comparative Examples 1 to 5 were obtained in the same manner as Example 1, except that the proportions of the acrylic type copolymer materials were changed to the proportions shown in Table 1.

Reference Example 6

Forming First Ink Receiving Layer

[0055] A coating solution for a first ink receiving layer of the following compounding was dissolved and dispersed in water, and this coating solution was coated on one side of a base material and was dried, whereby a first ink receiving layer was provided.

Coating Solution for First Ink Receiving Layer

[0056]

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Binder resin

Itaconic acid modifed PVA (trade name: KL-318 K; produced by Kuraray Co., Ltd.), 39 weight parts

Silica (trade name: Mizukasil P78D; produced by Mizusawa Industrial Chemicals Ltd.), 39 weight parts

Cationic dye fixing agent (trade name: Polyfix550; produced by Showa Highpolymer Co., Ltd.), 19.5 weight parts
 Magnesium chloride (trade name: Magnesium Chloride S; produced by Tomita Pharmaceutical Co., Ltd.), 2.5 weight parts

Preparation of Acrylic Type Copolymer

[0057] Next, materials for acrylic type copolymer of the following compounding were dispersed in water/isopropanol (2/1) so as to be solid concentration of 40% by weight, and 5.0% by weight of azoisobutyrontrile was added in this mixture as a polymerization initiator. Then these were heated at 80 to 90°C, whereby an acrylic type copolymer having a weight-average molecular weight of 15,000 to 20,000 was prepared. Here, a compounding proportion of acrylic type copolymer is shown by mole %.

Compounding of Acrylic Type Copolymer

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- A component
- Dimethylamino ethylmethacrylate, 47.6 mole %
- B component
 - 2-Hydroxy ethylmethacrylate, 23.8 mole %
 - 2-Hydroxy ethylacrylate, 23.6 mole %
 - C component
 - UV absorptivity monomer represented by the following chemical formula 10, 1.0 mole %

Chemical Formula 10

 Other component Acrylamide, 4.0 mole %

Forming Second Ink Receiving Laver

[0059] Next, a coating solution for a second ink receiving layer of the following compounding was coated on the above first ink receiving layer, and was dried, whereby a second ink receiving layer was provided. Therefore, a recording medium for ink jet printer according to the present invention was formed.

Coating Solution for Second Ink Receiving Layer

[0060]

- . The above acrylic type copolymer (solid concentration: 40% by weight), 10% by weight
- Colloidal Silica (trade name: Snowtex UP; produced by Nissan Chemical Industries, Ltd.; solid concentration: 39% by weight), 90% by weight
- Reference Examples 7 to 14, and Comparative Examples 6 to 11

[0661] Recording media for ink jet printers of Reference Examples 7 to 14 not according to the present invention and Comparative Examples 6 to 11 were obtained in the same manner as Reference Example 6, except that the proportions of the acrylic type copolymer materials were changed to the proportions shown in Table 1. Here, antioxidation monomer used in some Examples and Comparative Examples, and dimethoxy polyethyene glyculf if 1000 methacrytale as a copolymerizing component of acrylic type copolymer other than the A, B, and C components, are shown by the following chemical Enrulas 11 and 12. respectively.

Table 1

	A Cor	Component	B Component	ponent	C Component	ponenl		Other Additives	
	Ethylacrylate	Dimethylamino Ethylmethacrylate	Dimethylamino 2-Hydroxy Ethylmethacrylate Ethylmethacrylate	2-Hydroxy Ethylacrylate	UV Absorption Monomer	Antioxidation Monomer	Acrylamide	Acrylonitrile	Dimethoxy Polyethylene Glycol #1000 Methacrylate
Example 1	54.5	1	13.4	1	1.0	8.0	1	22.1	1
Example 2	54.5	-	2.7		7.4	1	_	35.4	1
Example 3	53.5	-	13.4	1	4.5	4.5	-	24.1	1
*Example 4	65.1	-	18.4	1	11.0	5.5	-	1	-
*Example 5	54.0	1	18.4	1	19.6	8.0	1	1	1
Example 6	1	47.6	23.8	23.6	1.0	1	4.0	1	1
*Example 7		44.3	22.3	22.1	7.5		3.8	ı	
Example 8	ı	43.8	21.8	21.6	9.5	1	4.0	ı	1
Example 9	1	44.3	22.3	22.1	4.75	4.75	3.8	1	,
Example 10	1	45.45	25.86	1	1	7.5	4.1	ı	17.09
*Example 11	1	44.95	24.86	1	ı	9.5	4.1	ı	16.59
Example 12	1	45.45	12.93	12.93	4.75	4.75	4.1	1	17.09
Example 13	ı	27.9	14.1	13.9	20.0	20.0	4.1	ı	1
Example 14	1	37.95	28.36	.1	20.0	1	4.1	-	65'6
Comparative Example 1	58.9	1	2.9	1	1	-	1	38.2	ı
Comparative Example 2	53.5	1	13.4	ı	1	-		33.1	1
Comparative Example 3	54.5	1	1	ı	ı	1	-	45.5	1
Comparative Example 4	54.0	_	-	1	19.6	8.0	-	18.4	1
Comparative Example 5	53.5	ı	ł	_	2.0	8.0	_	35.5	1
Comparative Example 6	1	86.5	1	ı	9.5	ı	4.0	ł	1
Comparative Example 7	1	33.1	-	-	4.75	4.75	4.1		55.3
Comparative Example 8	ı	32.1	ı	1	-	9.5	4.1	1	54.3
Comparative Example 9	1	626	-	_	-	-	4.1	1	_
Comparative Example 10	4	47.9	24.1	23.9	1	1	4.1	1	1
Comparative Example 11	1	47.95	38.36	1	-	`	4.1	1	65.6

*Reference Examples

Chemical Formula 11

Chemical Formula 12

[0062] Subsequently, with regard to the recording media for ink jet printers obtained in Examples 1-3 and Reference Examples 4-14 and the comparative recording media for ink jet printers obtained in Comparative Example 1 to 11, the objects for evaluation such as a color patch or the like were printed on the second ink receiving layer, using an ink jet printer (trade name: PM-700C; produced by Seiko Epson Corporation), thereby obtaining printed images. Light resistance, surface strength, and link absorptivity were evaluated by the means describbed below using these printer images.

Evaluation means

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Light resistance 1 (xenon lamp accelerated test)

[0063] As an exposure test, a magenta color patch on each recording medium for ink jet printers of the Example or the Comparative Example was irradiated by UV radiation at 90 kJ/m² under the conditions black panel temperature: 65°C: relative humility; 50%; radiation power of uttwoide at 340 m. 0.35 W/m², using a xenon whether-ometer (trade name: Ci-5000; produced by Atlas Electric Devices Co.). Then, the remaining ratio of refraction density was obtained by measuring refraction density of the exposed magenta color patch and the original, using a spectrophotometer (trade name: CRETAG SPM50; produced by Gretal Anabeth Corporation). The light resistance 1 was thereby evaluated.

Light resistance 2 (fluorescent lamp accelerated test)

[0064] As an exposure test, each recording medium for ink jet printers of the Example or the Comparative Example was irradiated at about 6 Wim² (at ultraviolet ray reages of 300 to 400 nm) for 150 hours, using a flourescent lample accelerated tester (trade name: iPHUV; produced by Atlas Electric Devices Co.). Then, the remaining ratio of reflection density was obtained by measuring refraction density of the exposed magenta color patch and the original, using a spectophothomster (trade name: GRETAG SPM50; produced by Gretag Macbeth Corporation), in the same manner as a xenon lamp accelerated test of the light resistance 2 was thereby evaluated.

Light resistance 3 (sunlight and real environment test)

[0065] Yellow, magenta, cyan, and black color patches were printed on each recording medium for lik jet printers of 5 the Example or the Comparative Example, and these color patches were left near a window facing south for about 1 month. Thereafter, the remaining ratios of the refraction density were obtained on these color patches, in the same manner as light resistance 1, and the light resistance 3 was evaluated by the average of the remaining ratio.

Surface strength (adhesive property)

[0066] A piece of cellophane tape was adhered on the second ink receiving layer formed images, and it was pulled off, whereby surface strength was evaluated according the following criteria.

Evaluation of surface strength

[0067]

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- A: cases where the problem was not observed at all in practice and surface strength was superior (nothing adhered to the cellophane tape)
- B: cases where the problem was not observed in practice and surface strength was superior (a few fragments
- adhered to the cellophane tape, but no part of the recorded image tore off)
- C: cases where surface strength was inferior in practice (at least a part of recorded image tore off)

Ink absorptivity

[0068] Images were printed on the recording sheet by an ink jet printer and the ink absorptivity was evaluated by observing multicolor bleeding and uncloic of bedering thereon. The evaluation was performed by comparing the ink absorptivities of genuine glossy papers (trade name: glossy paper for super-fine (thick-type) photoprint paper; produced by Seiko Epson Corporation) by visual inspection.

Evaluation of ink absorptivity

25 [0069]

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A: cases where the problem was not observed in all in practice and link absorptivity was superior (equal to or better) ple cases where the problem was not observed in practice and link absorptivity was superior (it was slightly inferior, but differences in the SCID image was not observed).

C. cases where ink absorptivity was inferior in practice.

[0070] These evaluated results are shown in Table 2.

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Table 2

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Ink Absorptivity	Ą	A	A	A	V	A	A	A	A	A	Ą	٨	В	В	A	∢	В	В	В	U	U	ပ	U	ပ	U
Surface Strength	A	A	A	¥	В	Ą	A	ď	A	A	A	ď	æ	В	В	В	ပ	U	U	U	O	O	O	0	U
Light Resistance 3 (%)	96	35	93	- 26	93	26	92	94	91	45	16	06	83	81	55	55	22	95	95	78	78	11	99	62	92 、
Light Resistance 2 Light Resistance (%)	95	94	92	92	94	16	93	94	91	93	06	93	. 81	82	51	54	20	06	93	76	78	77	69	92	11
Light Resistance 1 (%)	93	92	94	96	92	90	95	91	93	92	94	91	82	81	53	58	51	93	91	79	77	79	89	78	76
	Example 1	Example 2	Example 3	Example 4 *	Example 5 *	Example 6 *	Example 7 *	Example 8 *	Example 9 *	Example 10 *	Example 11 *	Example 12 💥	Example 13 *	Example 14 🗶	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8	Comparative Example 9	Comparative Example 10	Comparative Example 11

* Reference Example

[0071] As is apparent from the results in Table 2, every one of the recording media for ink jet printers according to the present invention, has superior properties. In addition, in Reference Example 5 in which the content of the Component is high, the surface strength was slightly deteriorated, and in Reference Examples 13 and 14 in which the content of the A and Components or the content of the Component deviates from a suitable range, any or all of the light resistance, surface strength, and ink absorptivity were slightly deteriorated, however, these deteriorations were not problems encountered in practice. In contrast, in the Components were

not completed, any or all of the light resistance, surface strength, and ink absorptivity were inferior. In particular, the surface strength and link absorptivity in Comparative Examples 3 to 11 were extremely inferior, and these recording media for ink to printers could not be used in oractice.

[0072] As explained above, according to the present invention, by including acrylic type copolymer in which at least three components of the A component: (metha)acrylate; the B component: hydroxyalkyl (metha)acrylate; and the C component: antioxidation monomer and/or ultraviolet ray absorptivity monomer are copolymerizing components, a recording medium for ink jet printers having superior recording properties for ink jet printers in which dear images having no blurring can be obtained by superior ink absorptivity and in which superior light resistance and surface strength are exhibited, can be formed. Furthermore, according to the present invention, by using the above specific copolymer, the moisture resistance in which color of images do not change or fade even if recorded images are left under high temperature and high humidity. can be also improved.

Claims

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- A recording medium for ink jet printers comprising an ink receiving layer provided on a base material, wherein said
 ink receiving layer contains acrylic type copolymer comprising four components (A): (meth)acrylate; (B) hydroxyalkyl
 (meth)acrylate; C: antioxidation monomer and/of uttlaviolet ray absorptivity monomer, and (D) acrylontifile.
- 2. A recording medium for ink jet printers as recited in claim 1, wherein said A component is alkylacrylate.
 - A recording medium for ink jet printers as recited in claim 2, wherein the content of said C component in said acrylic type copolymer is 1 to 20 mole %.
- 25 4. A recording medium for ink jet printers as recited in claim 2 or 3, wherein the content of said B component in said acrylic type copolymer is 1 to 25 mole %.
 - A recording medium for ink jet printers as recited in one of claims 2 to 4, wherein said ink receiving layer further contains pigment, and the compounding ratio of said binder resin and said pigment is 30: 70 to 95: 5 by weight ratio.
 - A recording medium for ink jet printers as recited in one of claims 2 to 5, wherein the content of said acrylic type copolymer in said binder resin is 30 to 100% by weight.
 - A recording medium for ink jet printers as recited in daim 1, wherein said A component is dialkytamino alkylmethacrylate when said ink receiving layer is provided as a most surface layer, said acrylic type copolymer further consisting of acrylamide as a copolymerizing component.
 - A recording medium for ink jet printers as recited in claim 7, wherein the content of said C component in said acrylic type copolymer is 0.5 to 10 mole %.
 - A recording medium for ink jet printers as recited in claim 7 or 8, wherein the content of said A component in said acrylic type copolymer is 30 to 60 mole %, and the content of said acrylamide is 2 to 7 mole %.
 - 10. A recording medium for ink jet printers as recited in one of claims 7 to 9, wherein the content of said B component in said acrylic type copolymer is 15 to 50 mole %.
 - 11. A recording medium for ink jet printers as recited in one of claims 7 to 10, wherein said ink receiving layer further contains pigment, and the compounding ratio of said acrylic type copolymer and said pigment is 5: 95 to 30: 70 by weight ratio.

Patentansprüche

Aufzeichnungsmedium für Tintenstrahldrucker, welches eine auf einem Trägermaterial vorgesehene Tintenaufnahmesschiet hin Arcyfopodymer der vier Komponenten: (A) (Meht)-Acrylat; (B) Hydroxyalky(meht-)acrylat; (C) Antioxidationsmonomer und/oder Ultravioletstrahlen absorbierendes Monomer: und (D) Acrylati enthält.

- 2. Aufzeichnungsmedium für Tintenstrahldrucker nach Anspruch 1, bei dem die Komponente A Alkylacrylat ist.
- Aufzeichnungsmedium für Tintenstrahldrucker nach Anspruch 2, bei dem der Gehalt an der Komponente C in dem Acrylcopolymer 1 bis 20 Mol-% beträgt.
- Aufzeichnungsmedium für Tintenstrahldrucker nach Anspruch 2 oder 3, bei dem der Gehalt an der Komponente B
 in dem Acrylcopolymer 1 bis 25 Mol-% beträgt.
- Aufzeichnungsmedium für Tintenstrahldrucker nach einem der Ansprüche 2 bis 4, bei dem die Tintenaufnahmeschicht zusätzlich Pigment enthält, und des gewichtsbezogene Mischverhältnis von Bindeharz zu Pigment 30:70 bis 95:5 beträgt.
 - Aufzeichnungsmedium für Tintenstrahldrucker nach einem der Ansprüche 2 bis 5, bei dem der Gehalt an dem Acrylcopolymer im Bindeharz 30 bis 100 Gew.-% beträgt.
- Aufzeichnungsmedium für Tintenstrahldrucker nach Anspruch 1, bei dem die Komponente A Dialkylaminoalkylmethacrylat ist, wenn die Tintenaufnahmeschicht als eine äußerste Oberflächenschicht vorgesehen ist, wobei eine zusätzliche opolymerisierende Komponente des Acry/copylmers aus Acrylamid besteht.
- Aufzeichnungsmedium für Tintenstrahldrucker nach Anspruch 7, bei dem der Gehalt an der Komponente C in dem Acrylcopolymer 0,5 bis 10 Mol-% beträgt.
 - Aufzeichnungsmedium für Tintenstrahldrucker nach Anspruch 7 oder 8, bei dem der Gehalt an der Komponente A in dem Acrylcopolymer 30 bis 60 Mol-% und der Gehalt an dem Acrylamid 2 bis 7 Mol-% beträgt.
 - Aufzeichnungsmedium für Tintenstrahldrucker nach einem der Ansprüche 7 bis 9, bei dem der Gehalt an der Komponente B in dem Acrylcopolymer 15 bis 50 Mol-% beträgt.
 - Aufzeichrungsmedium für Tintenstrahldrucker nach einem der Ansprüche 7 bis 10, bei dem die Tintenaufnahmeschicht zusätzlich Pigment enthält, und das gewichtsbezogene Mischverhältnis von Acrylcopolymer zu Pigment 5: 95 bis 30.70 beträgt.

Revendications

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- Matériau pour impression à jet d'encre comprenant une couche de réception d'encre fournie sur un matériau de base, dans lequel ladite couche recevant l'encre confient un copolymère de type acrylique comprenant quatre composants : (A) (méth)acrylate; (B) hydroxyalkly (méth)acrylate; (C) monomère anti-oxydation et/ou monomère d'absorption des rayons ultraviolets, et (D) acrylonitrile.
- 2. Matériau pour impression à jet d'encre selon la revendication 1, dans lequel le composant A est un alkylacrylate.
 - Matériau pour impression à jet d'encre selon la revendication 2, dans lequel la teneur dudit composant C dans ledit copolymère de type acrylique est de 1 à 20 % en moles.
- Matériau pour impression à jet d'encre selon la revendication 2 ou 3, dans lequel la teneur dudit composant B dans ledit copolymére de type acrylique est de 1 à 25 % en moles.
- Matériau pour impression à jet d'encre selon l'une des revendications 2 à 4, dans lequel ladite couche de réception d'encre contient en outre un pigment, et le taux de composition de ladite résine liante et dudit pigment est 30 : 70 à 95 : 5 en rapport pondéral.
 - Matériau pour impression à jet d'encre selon l'une des revendications 2 à 5, dans lequel la teneur dudit copolymère de type acrylique dans ladite résine liante est de 30 à 100 % en poids.
 - Matériau pour impression à jet d'encre selon la revendication 1, dans lequel le composant A est un dialitylamino-alsyméthacrylate lorsque ladite couche necevant l'encre est fournie comme une couche de surface principale, ledit copolymère de type acrylique se composant en outre d'acrylamide comme composant copolymérisant.

- Matériau pour impression à jet d'encre seion la revendication 7, dans lequel la teneur dudit composant C dans ledit copolymère de type acrylique est 0.5 à 10 % en moles.
- Matériau pour impression à jet d'encre selon l'une des revendications 7 et 8, dans lequel la teneur dudit composant A dans ledit copolymère de type acrylique et 30 à 60 % en moles, et la teneur dudit acrylamide est de 2 à 7 % en moles.

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- 10. Matériau pour impression à jet d'encre selon l'une des revendications 7 à 9, dans lequel la teneur dudit composant B dans ledit copolymère de type acrylique est de 15 à 50 % en moles.
- 11. Matériau pour impression à jet d'encre selon l'une des revendications 7 à 10, dans lequel ladite couche de réception d'encre contient en outre un pigment, et le taux, de composition dudit copolymère de type acrylique et dudit pigment est 5: 95 à 30: 70 en rapport pondére.